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TO

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1. Your reference

AA 1389 GB

2. Patent application number

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LONDON SW1Y 5BQ

Patents ADP number (if you know it)

If the applicant is a corporate body, give the
country/state of its incorporation

GB

00536268007

4. Title of the invention

IMPROVEMENTS IN EMISSION CONTROL

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom
to which all correspondence should be sent
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0391914 37001

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Country Priority application number
(if you know it) Date of filing
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7. If this application is divided or otherwise
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8. Is a statement of inventorship and of right
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YES

- a) any applicant named in part 3 is not an inventor, or
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Description	6
Claim(s)	2
Abstract	1
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Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

ONE

Request for substantive examination (Patents Form 10/77)

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11.

I/We request the grant of a patent on the basis of this application.

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Date 6 Feb 98

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AA 1389

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IMPROVEMENTS IN EMISSION CONTROL

The present invention concerns improvements in emissions control, and especially concerns improvements in selective catalytic reduction of NOx in waste gas streams such 5 as diesel engine exhausts or other lean exhaust gases such as from gasoline direct injection (GDI).

The technique named SCR (Selective Catalytic Reduction) is well established for 10 industrial plant combustion gases, and may be broadly described as passing a hot exhaust gas over a catalyst in the presence of a nitrogenous reductant, especially ammonia or urea. This is effective to reduce the NOx content of the exhaust gases by about 20-25% at about 250°C, or possibly rather higher using a platinum catalyst, although platinum catalysts tend to oxidise NH₃ to NOx during higher temperature operation. We believe that SCR systems have been proposed for NOx reduction for vehicle engine exhausts, especially large or heavy 15 duty diesel engines, but this does require on-board storage of such reductants, and is not believed to have met with commercial acceptability at this time.

We believe that if there could be a significant improvement in performance of SCR 20 systems, they would find wider usage and may be introduced into vehicular applications. It is an aim of the present invention to improve significantly the conversion of NOx in a SCR system, and to improve the control of other pollutants using a SCR system.

Accordingly, the present invention provides an improved SCR catalyst system, 25 comprising in combination an oxidation catalyst effective to convert NO to NO₂, a source of reductant fluid and downstream of said source, an SCR catalyst. A preferred system incorporates a particulate filter interposed between the oxidation catalyst and the source of reductant fluid.

The invention further provides an improved method of reducing NOx in gas streams, 30 comprising passing such gas stream over an oxidation catalyst under conditions effective to convert at least a portion of NO in the gas stream to NO₂, adding reductant fluid to the gas stream containing enhanced NO₂ to form a gas mixture, and passing the gas mixture over

referably, particulates are filtered out of the gas stream, desirably by particulate filter between the oxidation catalyst and the source of reductant

5 The invention is believed to have particular application to the exhausts from heavy duty diesel engines, especially vehicle engines, eg truck or bus engines, but is not to be regarded as being limited thereto. Other applications might be LDD (light duty diesel), GDI, CNG (compressed natural gas) engines, ships or stationary sources. For simplicity, however, the majority of this description concerns such vehicle engines.

10 We have surprisingly found that a "pre-oxidising" step, which is not generally considered necessary because of the low content of CO and unburnt fuel in diesel exhausts, is particularly effective in increasing the conversion of NO_x to N₂ by the SCR system. Desirably, the NO₂/NO ratio is adjusted according to the present invention to the most beneficial such ratio for the particular SCR catalyst and CO and hydrocarbons are oxidized prior to the SCR catalyst. Thus, our preliminary results indicate that for a transition metal/zeolite catalyst it is desirable to convert all NO to NO₂, whereas for a rare earth-based catalyst, a high ratio is desirable providing there is some NO, and for other transition metal-based catalysts gas mixtures are notably better than either substantially only NO or NO₂.
15
20 Even more surprisingly, the incorporation of a particulate filter permits still higher conversions of NO_x.

25 The oxidation catalyst may be any suitable catalyst, and is generally available to those skilled in art. For example, a Pt catalyst deposited upon a ceramic or metal through-flow honeycomb support is particularly suitable. Suitable catalysts are e.g. Pt/Al₂O₃ catalysts, containing 1-150g Pt/ft³ (0.035-5.3g Pt/litre) catalyst volume depending on the NO₂/NO ratio required.

30 The source of reductant fluid conveniently uses existing technology to inject fluid into the gas stream. For example, in the tests for the present invention, a mass controller was used to control supply of compressed NH₃, which was injected through an annular

injector ring mounted in the exhaust pipe. The injector ring had a plurality of injection ports arranged around its periphery. A conventional diesel fuel injection system including pump and injector nozzle has been used to inject urea by the present applicants. A stream of compressed air was also injected around the nozzle; this provided good mixing and cooling.

5

The reductant fluid is suitably NH₃, but other reductant fluids including urea, ammonium carbamate and hydrocarbons including diesel fuel may also be considered. Diesel fuel is, of course, carried on board a diesel-powered vehicle, but diesel fuel itself is a less selective reductant than NH₃, and is presently not preferred.

10

Suitable SCR catalysts are available in the art. A preferred catalyst at present is a V₂O₅/WO₃/TiO₂ catalyst, supported on a honeycomb support. Although such a catalyst has shown good performance in the tests described hereafter and is commercially available, we have found that sustained high temperature operation can cause catalyst deactivation. Heavy duty diesel engines, which are almost exclusively turbocharged, can produce exhaust gases at greater than 500°C under conditions of high load and/or high speed, and such temperatures are sufficient to cause catalyst deactivation. In one embodiment of the invention, therefore, cooling means is provided upstream of the SCR catalyst. Cooling means may suitably be activated by sensing high catalyst temperatures or by other, less direct, means, such as determining conditions likely to lead to high catalyst temperatures. Suitable cooling means include water injection upstream of the SCR catalyst, or air injection, for example utilising the engine turbocharger to provide a stream of fresh intake air by-passing the engine. We have observed a loss of activity of the catalyst, however, using water injection, and air injection by modifying the turbocharger leads to higher space velocity over the catalyst which tends to reduce NO_x conversion. Preferably, the preferred SCR catalyst is maintained at a temperature from 160°C to 450°C.

We believe that in its presently preferred embodiments, the present invention may depend upon an incomplete conversion of NO to NO₂. Desirably, therefore, the oxidation catalyst, or the oxidation catalyst together with the particulate trap if used, yields a gas stream entering the SCR catalyst having a ratio of NO to NO₂ of from about 4:1 to about 1:3

by vol, for the commercial vanadia-type catalyst. As mentioned above, other SCR catalysts perform better with different NO/NO₂ ratios. We do not believe that it has previously been suggested to adjust the NO/NO₂ ratio in order to improve NOx reduction.

5 A preferred embodiment of the present invention incorporates a particulate trap downstream of the oxidation catalyst. We discovered that soot-type particulates may be removed from a particulate trap by "combustion" in the presence of NO₂. In effect, the incorporation of such a particulate trap serves to clean the exhaust gas of particulates without causing accumulation, with resultant blockage or back-pressure problems, whilst 10 simultaneously reducing a proportion of the NOx. Suitable particulate traps are generally available, and are desirably of the type known as wall-flow filters.

15 A particularly interesting possibility arising from the present invention has especial application to light duty diesel engines (car and utility vehicles) and permits a significant reduction in volume and weight of the exhaust gas after-treatment system.

20 Several tests have been carried out in making the present invention. These are described below as examples of the invention, and are supported by results shown in graphical form in the attached drawings.

25 A commercial 10 litre turbocharged heavy duty diesel engine on a test-bed was used for all the tests described herein.

Test 1 - Comparative

30 A conventional SCR system using a commercial V₂O₅/WO₃/TiO₂ catalyst, was adapted and fitted to the exhaust system of the engine. NH₃ was injected upstream of the SCR catalyst at varying ratios. The NH₃ was supplied from a cylinder of compressed gas and a conventional mass flow controller used to control the flow of NH₃ gas to an experimental injection ring. The injection ring was a 10cm diameter annular ring provided with 20 small injection ports arranged to inject gas in the direction of the exhaust gas flow.

NO_x conversions were determined by fitting a NO_x analyser before and after the SCR catalyst and are plotted against exhaust gas temperature in Figure 1. Temperatures were altered by maintaining the engine speed constant and altering the torque applied. It can readily be seen that at low temperatures, corresponding to light load, conversions are about 5 25%, and the highest conversions require stoichiometric (100%) addition of NH₃ at catalyst temperatures of from 325 to 400°C, and reach about 90%. However, we have determined that at greater than about 70% of stoichiometric NH₃ injection, NH₃ slips through the SCR catalyst unreacted, and can cause further pollution problems.

10 Test 2

The test rig was modified by inserting into the exhaust pipe upstream of the NH₃ injection, a commercial platinum oxidation catalyst of 10.5 inch diameter and 6 inch length (26.67cm diameter and 15.24cm length) containing 10g Pt/ft³ (= 0.35g/litre) of catalyst 15 volume. Identical tests were run, and it was observed from the results plotted in Figure 2, that even at 225°C, the conversion of NO_x has increased from 25% to >60%. The greatest conversions were in excess of 95%. No slippage of NH₃ was observed in this test nor in the following test.

20 Test 3

The test rig was modified further, by inserting a particulate trap before the NH₃ injection point, and the tests run again under the same conditions. The results are plotted and shown in Figure 3. Surprisingly, there is a dramatic improvement in NO_x conversion, 25 to above 90% at 225°C, and reaching 100% at 350°C. Additionally, of course, the particulates which are the most visible pollutant from diesel engines, are also controlled.

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Test 4

An R49 test with 80% NH₃ injection was carried out over a V₂O₅/WO₃/TiO₂ SCR catalyst. This gave 67% particulate, 89% HC and 87% NO_x conversion; the results plotted
5 in Figure 4.

CLAIMS

1. An improved SCR system for treating combustion exhaust gas containing NOx, comprising in combination an oxidation catalyst effective to convert at least a portion of NO in said NOx to NO₂, a source of reductant fluid and an SCR catalyst.
2. An SCR system according to claim 1, wherein the reductant fluid is NH₃.
3. An SCR system according to claim 1 or 2, wherein the oxidation catalyst is a platinum catalyst carried on a through-flow honeycomb support.
4. An SCR system according to claim 1, 2 or 3, comprising further a particulate filter interposed between the oxidation catalyst and the source of reductant fluid.
5. An SCR system according to claim 4, wherein said particulate filter is a wall-flow filter.
6. A diesel engine provided with an SCR system according to any one of claims 1 to 5.
7. A light duty diesel engine according to claim 6, wherein the volume of the exhaust gas after-treatment system is reduced.
8. A method of reducing NOx in gas streams, comprising passing such gas stream over an oxidation catalyst under conditions effective to convert at least a portion of NO in the gas stream to NO₂, adding reductant fluid to the gas stream containing enhanced NO₂ to form a gas mixture, and passing the gas mixture over an SCR catalyst under NOx reduction conditions.
9. A method according to claim 8, wherein said gas stream is the exhaust from a diesel, GDI or CNG engine.

10. A method according to claim 8 or 9, comprising the additional step of filtering particulates from a diesel exhaust gas stream downstream of the oxidation catalyst.

11. A method of improving the conversion of NO_x in exhaust gas streams using an SCR catalyst and a reductant, comprising adjusting the NO to NO₂ ratio to a level pre-determined to be optimum for said catalyst, by passing said exhaust gas through an oxidation catalyst.

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IMPROVEMENTS IN EMISSION CONTROL

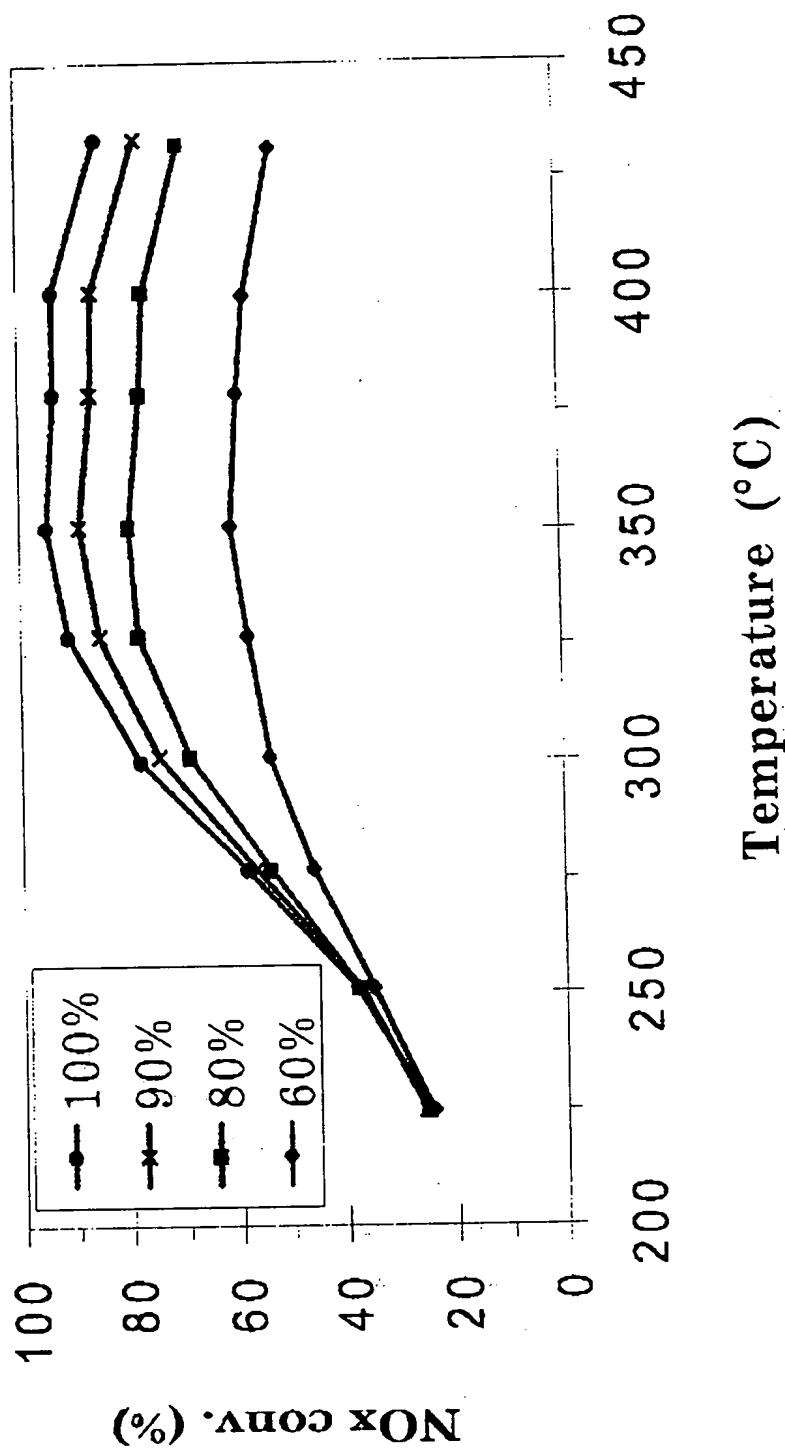
Abstract of the Invention

5 A system for NOx reduction in combustion gases, especially from diesel engines, incorporates an oxidation catalyst to convert at least a portion of NO to NO₂, a source of reductant such as NH₃, and an SCR catalyst. A preferred system uses a particulate filter before the SCR catalyst. Considerable improvements in NOx conversion are observed.

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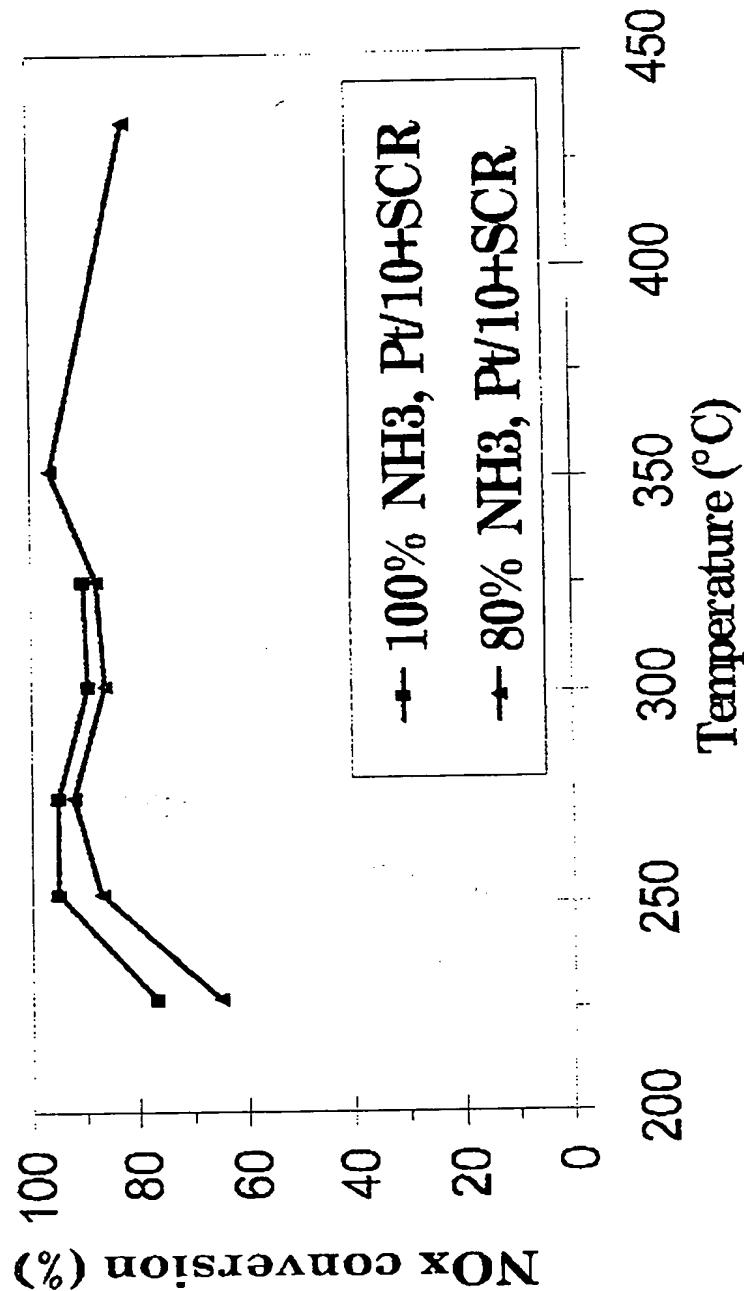
NO_x Conversion vs T for different amounts of NH_3 Injection
 NH_3 addition calculated at 1:1 NH_3/NO and 4:3 NH_3/NO_2
and 60-100% Injection of the calculated amount of NH_3 .



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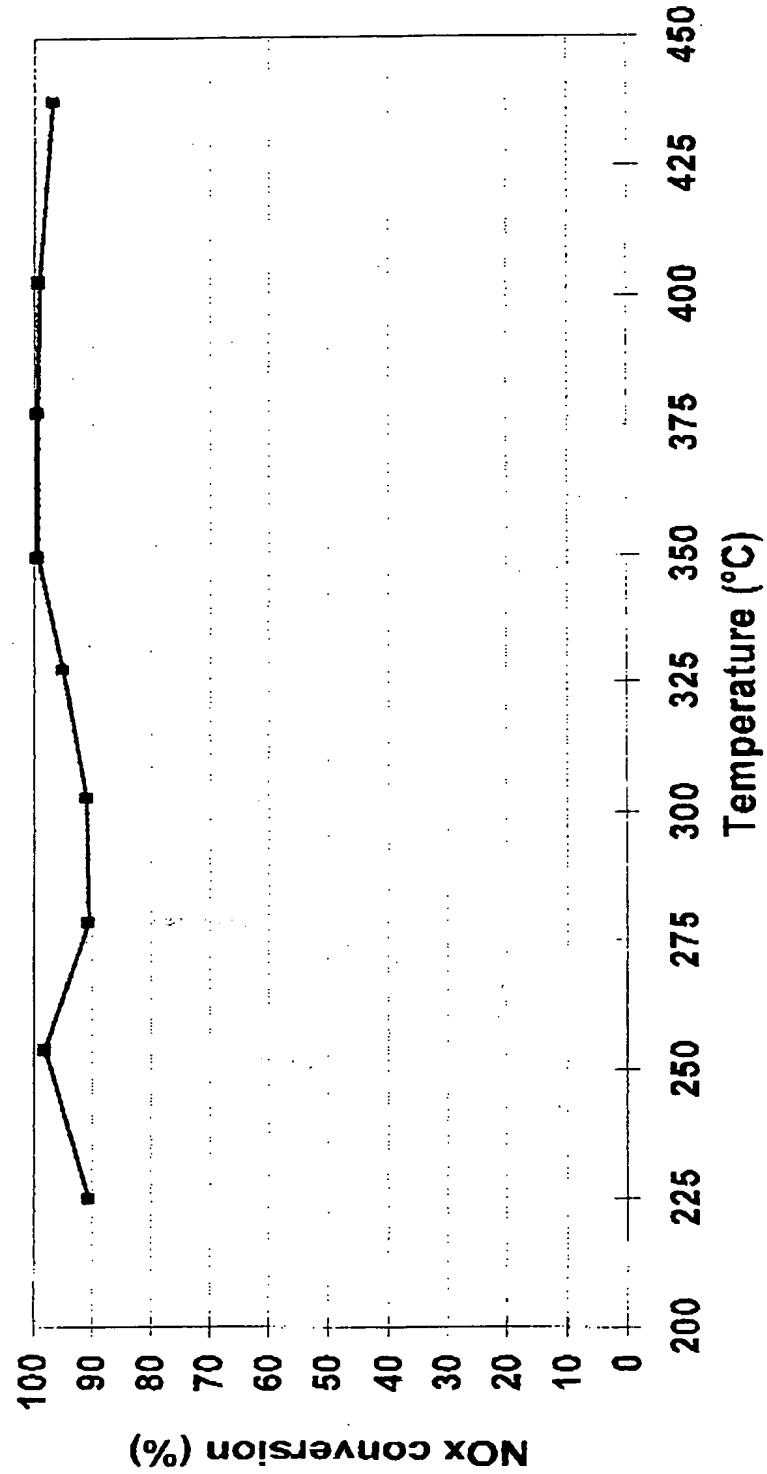
Oxi-cat + SCR-cat



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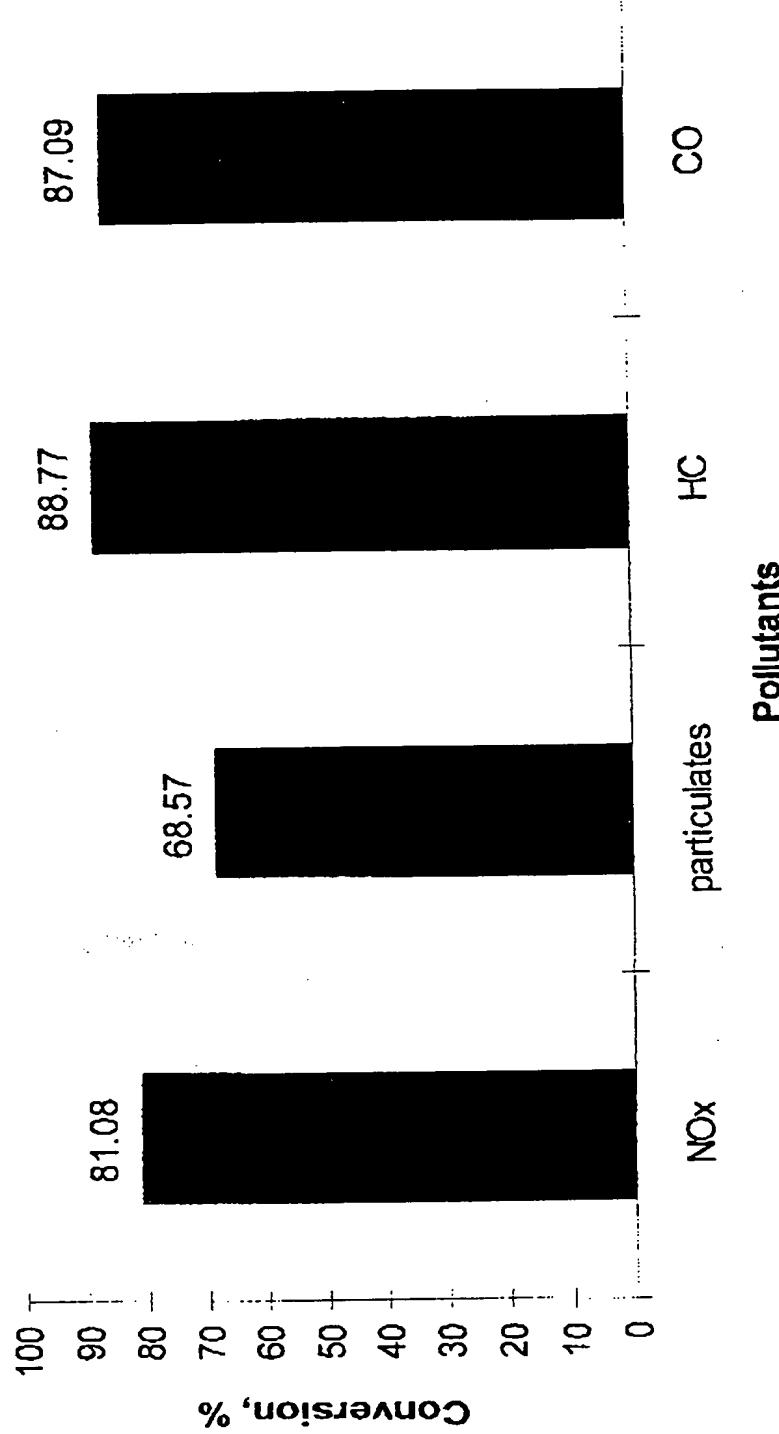
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NO_x conversion over Vanadium based SCRT catalyst system
100% NH₃ injection, (SV: 40000 - 70000)



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R49 Test Results: SCRT-System
80% NH3 injection



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Johnson Matthey

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